Evidence for hole and electron trapping in plasma deposited ZrO$_2$ thin films

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We have observed electron and hole trapping phenomena in thin films of ZrO$_2$ obtained by plasma assisted deposition. Limited thickness dependent measurements suggest that the holes are trapped uniformly through the film while the electrons trap at the ZrO$_2$/Si interface. Relaxation of the trapped holes occurs rapidly after removal of negative stress ($\sim$90% in 15 min), while electron relaxation postpositive stress occurs more slowly ($\sim$10% in 100 min). Cycling between states of positive trapped charge and negative trapped charge by application of the appropriate stressing voltage was observed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1401796]

Various dielectric materials having relative permittivities substantially greater than SiO$_2$ ($\sim$3.9) are presently under investigation for use in future microelectronics circuits. Applications include memory cell dielectrics in dynamic random access memories (DRAMs), coupling capacitor dielectrics in wireless technologies, and gate oxides in metal–oxide–semiconductor field effect transistors (MOSFETs). Various criteria need to be addressed in the choice of the dielectric,[1] only one of which is the magnitude of the dielectric constant. We have recently begun a study of the physical properties of one such dielectric, ZrO$_2$, which we have obtained by plasma assisted chemical vapor deposition (PECVD). The as-deposited films are essentially amorphous (though some evidence for crystallinity is present) and the relative permittivity is typically $\sim$20. In the present work we report the results of a series of electrical measurements on as-deposited films which show interesting evidence for hole and electron trapping in these films.

Films of ZrO$_2$ were deposited on p-type $\langle 100 \rangle$ Si wafers using a microwave excited (2.45 GHz) electron cyclotron resonance PECVD reactor, the substrate temperature during deposition was nominally room temperature. Prior to introduction into the reactor, the Si wafers were dipped in 49% HF acid and blown dry without subsequent washing in distilled water. We have previously found that this process leaves the Si surface native oxidation resistant for extended times (up to several hours). The Zr containing source gas molecules were obtained from a liquid Zr butoxide [Zr(OC$_4$H$_9$)$_4$] source heated to $\sim$50 °C with gas delivery lines heated to 87 °C. The vapor pressure of the butoxide in the reactor was 0.2 mTorr. Oxygen was introduced into the reactor at a pressure of $\sim$1 mTorr. Typical microwave powers were $\sim$500 W yielding deposition rates of ZrO$_2$ $\sim$3 nm min^{-1}. Two film thicknesses were used in the present experiments, 40 and 70 nm. Gold electrodes were deposited

onto the deposited ZrO$_2$ film using a shadow mask technique, the dot diameter was typically 200 μm. Oxide film thicknesses were ascertained by single wavelength (632.8 nm) ellipsometry. The refractive index of the films was typically 1.75–1.78.

Rutherford backscattering analysis (RBA) of the content of the deposited films was carried out[2] using a 2.275 MeV He^{++} beam for two backscattering angles, 102° and 160° to obtain depth profile information. The O, Zr, and C depth profiles in the deposited layer obtained by deconvolution of the RBA data is shown in Fig. 1. The Si signal arises from the substrate. A Zr:O ratio of 1:2 was obtained with a quoted concentration uncertainty of 1% for Zr and 4% for O. Clearly, using the two backscattering angle technique it was possible to determine that some C was present on the surface of the film but not (within quoted experimental accuracy of 7%) in the bulk of the film.

Quasi-static and high frequency (100 kHz) MOS capacitance/voltage measurements[3] [$C(V)$] and current/voltage [$I(V)$] measurements were carried out using a Keithley Instruments system. Since the MOS capacitors had not been subjected to the standard interface passivating forming gas anneal the interface state density was high ($\sim$10^{12} states eV^{-1} cm^{-2}). Current/voltage curves obtained for 70 nm thick ZrO$_2$ films are shown in Fig. 2. One observes that for an electric field of 1 MV cm^{-1} (corresponding to $V_{GS} \pm 7$ V) the film leakage current density is $\leqslant 2 \times 10^{-6}$ A cm^{-2}. This value is acceptable though larger than found by other authors studying ZrO$_2$/SiO$_2$ stacks where the ZrO$_2$ was deposited by atomic layer CVD[4] (ALCVD) and ALCVD ZrO$_2$ films deposited on nitrided Si subrstates.[5] However, in the SiO$_2$ stack case[4] the SiO$_2$ layer at the Si/dielectric interface reduced the overall relative permittivity to $\sim$15 and would certainly have also reduced charge injection by introducing a significant barrier height. Similarly, reductions in dielectric constant occurred for the nitrided interface studies.[5]

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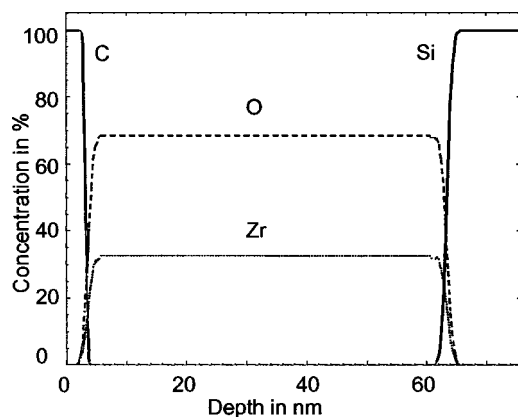| 16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
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FIG. 1. Depth profiles of O, Zr, C, and Si deduced from Rutherford back-scattering data on an approximately 65 nm thick ZrO_2 film deposited at room temperature using microwave plasma enhanced chemical vapor deposition. The relative accuracy quoted for the different concentrations was 7% (C), 4% (O), 1% (Zr), and 1% (Si), all concentrations being in atomic percent.

FIG. 3. Flatband voltage shift as a function of stress time for 40 and 70 nm thick ZrO_2 films subjected to positive and negative 1 MV cm^{-1} electric fields. Cycling of the effect was observed by applying first one sense of stress then applying the opposite sign and magnitude of stress.

During the process of electrical characterization it was realized that charging effects were occuring and that the nature of the charging depended upon the sign of the voltage applied to the gate electrode during stressing. A series of measurements of the flatband voltage shift of the MOS capacitors was carried out as a function of sign of the gate electrode voltage and time. The data for the two film thicknesses, 40 and 70 nm, is presented in Fig. 3. The gate electrode voltage (V_{GS}) was chosen for each film so as to provide a stressing electric field of 1 or -1 MV cm^{-1}. After application of the stressing field for the chosen time, the $C(V)$ curve was scanned rapidly ($\sim$20 s) and the stressing field then reapplied. We observe that a positive polarization resulted in a positive flatband voltage shift whereas negative polarization resulted in a negative shift. In order to further study kinetics of the trapped charge we performed measure-
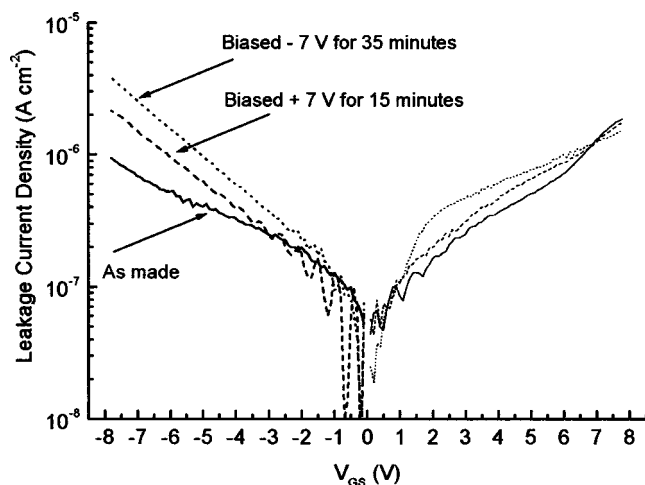

FIG. 2. Leakage current density vs gate electrode/substrate voltage (V_{GS}) for a 70 nm thick ZrO_2 film with a Au electrode. The different curves were obtained for as-made samples (—), samples first subjected to a 7 V V_{GS} bias for 15 min before sweeping (---), and samples first subjected to a -7 V V_{GS} bias for 35 min before sweeping (...). Though the stressing resulted in significant positive or negative flatband voltage shift, there appeared to be very little effect on the $I(V)$ curves.
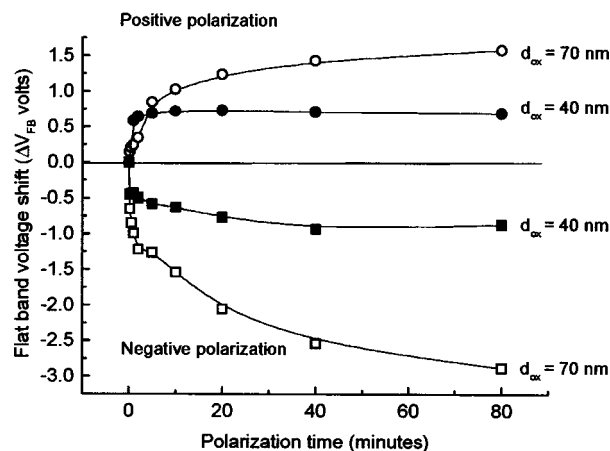
ments in which an electric field of 1 or -1 MV cm^{-1} was applied for a period of 30 min and the $C(V)$ curve then measured as a function of time. The variation of the flatband voltage shift (with respect to the unstressed value) as a function of time after polarization is shown in Figs. 4(a) and 4(b), during this "relaxation" time the gate electrode of the capacitor was left floating. In the former case, a positive polarization had been applied whereas in the latter, the polarization was negative. From Fig. 4(b) we see that the negative flatband voltage relaxes rather rapidly whereas the positive shift [Fig. 4(a)] relaxes considerably slower. We observe that the flatband voltage shift resulting from trapped positive charge decays to 10% of its maximum value in approximately 15 min. The flatband voltage shift due to negative trapped charge decays by only 10% in $\sim$100 min. We also note that the capacitors could be cycled (electrically speaking) and that extended positive polarization always resulted in negative charge trapping while negative voltage stressing resulted in positive charge trapping.

The flatband voltage shift due to charge injected due to electrical stressing may be written as[3]

$$\Delta V_{FB} = -[1/C_{ox}](1/d_{ox}) \int x\rho(x)dx, \quad (1)$$

where C_{ox} is the oxide capacitance, d_{ox} the oxide thickness, and $\rho(x)$ the spatial charge density inside the oxide. The integral limits are taken from 0 to d_{ox} measured from the gate electrode. It is clear that a positive charge density results in a negative flatband voltage shift while the inverse is true for negative charge. In consequence, Fig. 3 indicates that application of a positive bias to the gate electrode results in the trapping of negative charge in the dielectric. Similarly, negative bias results in the introduction of positive charge in the oxide. In Fig. 2 we show the standard $I(V)$ plots on capacitors subjected to 7 V stress for 15 min before sweeping and -7 V for 35 min before sweeping. Though in Fig. 3 we see that such polarizations modify significantly the trapped charge, there are no dramatic changes in the $I(V)$ plots for samples containing trapped charge.
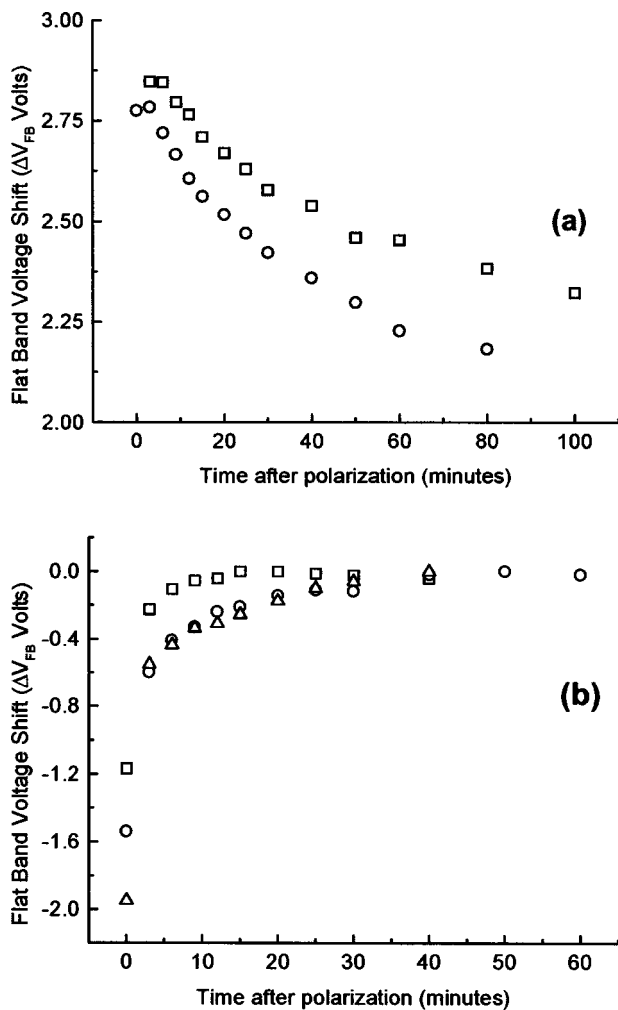
FIG. 4. (a) Time dependence of the flatband voltage due to trapped negative charge in a 70 nm thick sample stressed for 30 min in an applied electric field of 1 MV cm^{-1}. (b) Time dependence of the flatband voltage shift in the same sample subjected initially to a -1 MV cm^{-1} electric field for 30 min. The electrodes were left floating during the relaxation process. The different symbols in (a) and (b) correspond to different samples on the same wafer.

From the observations reported in Fig. 3 we conclude that positive bias stressing results in electron injection from the Si substrate into the oxide. Negative stressing appears to induce positive charge injection and trapping and this must also result from the substrate/oxide interface, the holes are not injected from the metal gate electrode. Assuming Eq. (1)

with a uniform distribution of charge $\rho_u(x)$ throughout the oxide we can integrate to deduce $\Delta V_{FB} \propto d_{ox}^2$, whereas if the trapped charge $\rho_\delta(x)$ is localized in a region of thickness δ at the oxide/Si interface we have $\Delta V_{FB} \propto d_{ox}\delta$. From Fig. 3, although we have data for only two thicknesses of oxide, we appear to observe negative charge trapping which is linear in oxide thickness and positive charge trapping which varies as the square of the oxide thickness. That is to say, positive charge traps uniformly throughout the oxide volume while negative charge traps close to the substrate/oxide interface. This observation allows us to conclude, account taken of the limited data, that the positive and negative trapped charge does not originate from a single amphoteric trap in the oxide but is due to distinctly different trapping sites. The kinetics of discharging of the traps shown in Figs. 4(a) and 4(b) are consistent with positively charged traps which are very shallow and may relax rapidly while the negatively charged traps appear to be somewhat energetically deeper and more stable.

From the flatband voltage shift data shown in Fig. 3 we can estimate the densities of trapped charge per cm^2. For the case of negative trapped charge we deduce the density of trapped electrons to be $\sim 2.4 \times 10^{12}$ cm^{-2}, a value reasonably close to that found[4] in ALCVD gate stacks (1.5×10^{12} cm^{-2}) following cycling of the $C(V)$ curve. In the case of the uniformly distributed positive trapped charge, the effective charge density per cm^{-2} varies with the oxide thickness. For the case of the 70 nm thick oxide the value is 4.8×10^{12} cm^{-2}.

We have obtained evidence for electrical stress induced hole and electron trapping in films of ZrO$_2$ deposited by microwave PECVD. The charges can be cycled by the application of the appropriate sign of electrical stress. Time dependent relaxation measurements suggest that the holes are more weakly bound than the electrons. More detailed measurements are in progress to characterize the charge trapping and the nature of the charge traps.

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